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Locating and Estimating Air Emissions from Sources of Chromium. Supplement

Midwest Research Inst., Cary, NC

Prepared for:

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16. ABSTRACT

To assist groups inventorying air emissions of potentially toxic substances, EPA is preparing a series of documents that compiles available information on sources and emissions of toxic substances. This document deals specifically with methods to estimate chromium (Cr^{+6}) emissions from cooling towers and electroplating operations.

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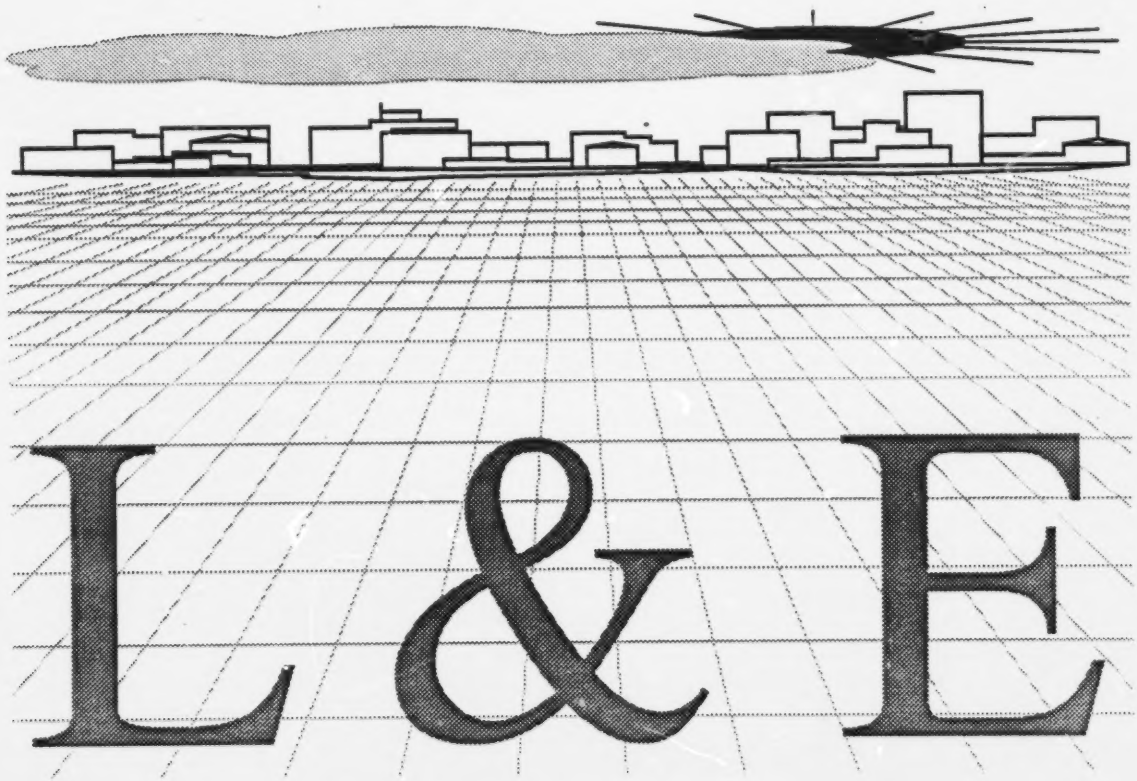
Note: The material herein on electroplating, chromic acid anodizing and cooling towers supersedes the material in EPA-450/4-84-007g.



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SUPPLEMENT

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Office of Air Quality Planning and Standards
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1.0 PURPOSE OF DOCUMENT

The U. S. Environmental Protection Agency (EPA), States, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, very little information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents that compiles available information on the sources and emissions of these substances. This document was prepared as a supplement to a previous EPA document that addressed chromium emissions, "Locating and Estimating Air Emissions From Sources of Chromium," EPA-450/4-84-007g. The supplement updates technical information and presents new emission data upon which emission factors are based for chromium emissions from cooling towers and chromium electroplating operations. The reader should use both the original document and this supplement to obtain the most complete assessment of emissions from these two sources of chromium emissions. The information in this supplement was obtained by EPA's Emission Standards Division for use in development of National Emission Standards for a Hazardous Air Pollutant (NESHAP) for chromium used in electroplating operations and for regulation of chromium emissions from comfort cooling towers under the Toxic Substances Control Act.

The reader is strongly cautioned against using the emissions information contained in the original document or this supplement to develop an exact assessment of emissions from any particular facility. Because of insufficient data, no estimate can be made of the error that could result when these factors are used to calculate emissions from any given facility. It is possible, in some extreme cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment, and operating practices. Thus, in situations where an accurate

assessment of chromium emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test and/or material balance should be considered as the best means to determine air emissions directly from an operation.

Possible sources of plant-specific information that would be useful in estimating air emissions of hexavalent chromium include the National Air Toxics Information Clearinghouse database maintained by EPA or the Toxics Release Inventory (TRI) data resulting from Section 313 of the Superfund Amendments and Reauthorization Act (SARA). In the absence of specific information about the locations of facilities, State Departments of Commerce, trade associations, or references such as the Thomas Register of American Manufacturers may be sources of information.

2.0 OVERVIEW OF DOCUMENT CONTENTS

This section outlines the information presented in the remaining sections of this report and indicates whether the information is new or whether it is a revision of information presented in the original document.

Section 3.1 presents process descriptions for five kinds of plating/anodizing operations. New information is included for decorative chromium electroplating of plastics, chromic acid anodizing, and trivalent chromium plating. Additional process information is provided to supplement the discussion of hard and decorative chromium electroplating presented in the original document. New emission data are presented for hard and decorative chromium electroplating operations; the results of an engineering mass balance to obtain an emission estimate for chromic acid anodizing are also presented. A significant change from the original document is in the format of the chromium emission factors for hard and decorative plating operations, which have changed from kilograms per hour per square foot of tank area to milligrams per ampere-hour. Supplemental information has been included on emission control techniques for reduction of chromic acid mist from plating operations. New information is presented on nationwide chromium emission estimates for three types of plating operations: hard plating, decorative plating, and chromic acid anodizing.

Section 3.2 presents updated information about the distribution of industrial process cooling towers that use chromium-based water treatment chemicals and presents new information about comfort cooling towers. New information also is presented on emission reduction techniques for chromium emissions from cooling towers. New emission data are presented for cooling towers equipped with low- and high-efficiency drift eliminators. A significant change from the original document is in the format of the chromium emission factor, which has changed from picograms per joule of thermal energy input to the power plant associated with the cooling tower to percentage of the recirculating chromium that is emitted. New information is presented on nationwide chromium emission estimates for industrial cooling towers in eight industries.

Section 4.0 summarizes the procedures used for source sampling and analysis of chromium in emission streams from electroplating operations and cooling towers.

3.0 CHROMIUM EMISSION SOURCES

3.1 CHROMIUM ELECTROPLATING AND CHROMIC ACID ANODIZING OPERATIONS

3.1.1 Background Information

Plating and anodizing operations range in size from small shops, with one or two tanks that are operated only a few hours per week, to large shops with several tanks that are operated 24 hours per day, 7 days per week. Many plating and anodizing operations are captive shops that perform chromium electroplating or chromic acid anodizing as one operation within or for a manufacturing facility, while others are job shops that provide custom plating or anodizing services for many different clients. Captive and job shops may perform hard or decorative chromium plating or chromic acid anodizing or any combination of these three operations.

The estimated number of electroplating shops nationwide is 1,540 hard chromium plating facilities and 2,800 decorative chromium plating facilities.[1] The estimated number of chromic acid anodizing shops nationwide is 680.[2] Electroplating and anodizing shops typically are located in or near industrial centers in areas of high population density. States with large numbers of chromium electroplaters include California, Illinois, Massachusetts, Michigan, New York, Ohio, and Pennsylvania.

3.1.1.1 Hard Chromium Electroplating of Metals. In hard plating, a relatively thick layer of chromium is deposited directly on the base metal (usually steel) to provide a surface with wear resistance, a low coefficient of friction, hardness, and corrosion resistance, or to build up surfaces that have been eroded by use.[3] Hard plating is used for items such as hydraulic cylinders and rods, industrial rolls, zinc die castings, plastic molds, engine components, and marine hardware.

Tanks used for hard chromium electroplating usually are constructed of steel and lined with a polyvinyl chloride sheet or plastisol. The anodes, which are insoluble, are made of a lead alloy that contains either tin or antimony. The substrate to be plated, the cathode, is suspended from a plating rack that is connected to the cathode bar of the rectifier. The plating rack may be loaded in the tank manually, by a hoist, or by an automatically controlled hoist system.

The plating tanks typically are equipped with some type of heat exchanger. Mechanical agitators or compressed air supplied through pipes on the tank bottom provide uniformity of bath temperature and composition. Chromium electroplating requires constant control of the plating bath temperature, current density, plating time, and bath composition.

Hexavalent chromium plating baths are the most widely used baths to deposit chromium on metal. Hexavalent chromium baths are composed of chromic acid, sulfuric acid, and water. The chromic acid is the source of the hexavalent chromium that reacts and deposits on the metal and that is emitted to the atmosphere. The sulfuric acid in the bath catalyzes the chromium deposition reactions. Typical operating parameters are given in Table 1.[4]

The evolution of hydrogen gas from chemical reactions at the cathode consumes 80 to 90 percent of the power supplied to the plating bath, leaving the remaining 10 to 20 percent for the deposition reaction. When the hydrogen gas evolves, it entrains chromic acid and causes misting at the surface of the plating bath.

3.1.1.2 Decorative Chromium Electroplating of Metals. In decorative plating, the base material (e.g., brass, steel, aluminum, or plastic) generally is plated with a layer of nickel followed by a relatively thin layer of chromium to provide a bright surface with wear and tarnish resistance. Decorative plating is used for items such as automotive trim, metal furniture, bicycles, hand tools, and plumbing fixtures. The purpose of decorative chromium plating is to achieve a combination of the following surface properties:

1. Blue-white color;
2. High reflectivity;
3. Tarnish resistance;
4. Corrosion resistance;
5. Wear resistance; and
6. Scratch resistance.[5]

Decorative electroplating baths operate on the same principle as that described for the hard chromium plating process: the metal substrate is immersed in a plating solution, and direct current is passed from the

TABLE 1. TYPICAL OPERATING PARAMETERS FOR HARD CHROMIUM ELECTROPLATING

Plating thickness, μm (mil)	1.3-762 (0.05-30)
Plating time, min[a]	20-2,160
Chromic acid concentration, g/ℓ (oz/gal)[b]	225-375 (30-50)
Temperature of solution, °C (°F)	49-66 (120-150)
Voltage, volts	c
Current, amperes (A)	d
Current density, A/m^2 (A/ft^2)[e]	1,600-6,500 (150-600)

[a] min. = minutes.
[b] g/ℓ = grams per liter, oz/gal = ounces per gallon.
[c] Depends on the distance between the anodes and the items being plated.
[d] Depends on the amount of surface area plated.
[e] A/m^2 = amperes per square meter (square foot) of surface area plated.

anode through the plating solution causing the desired metal (copper, nickel, chromium) to deposit out of the solution onto the metal substrate (cathode).

Decorative chromium plating requires shorter plating times and operates at lower current densities than does hard chromium plating to achieve the desired properties of the chromium plate. Some decorative chromium plating operations use fluoride catalysts instead of sulfuric acid because fluoride catalysts, such as fluosilicate or fluoborate, have been found to produce higher bath efficiencies.[6] Typical operating parameters are shown in Table 2.[7]

3.1.1.3 Decorative Chromium Electroplating of Plastics. Most plastics that are electroplated with chromium are formed from the polymer composed of acrylonitrile, butadiene, and styrene (ABS).[8] The process for chromium electroplating of ABS plastics consists of the following steps:

1. Chromic acid/sulfuric acid etch;
2. Dilute hydrochloric acid dip;
3. Colloidal palladium activation;
4. Dilute hydrochloric acid dip;
5. Electroless nickel plating or copper plating; and
6. Chromium electroplating cycle.

After each process step, the plastic is rinsed with water to prevent carry-over of solution from one bath to another. The chromic acid/sulfuric acid etch solution (see Table 3) renders the ABS surface hydrophilic and modifies the surface to provide adhesion for the metal coating.[9] The dilute hydrochloric acid dips are used to clean the surface and remove palladium metal from the plating rack, which is insulated with a coating of polyvinyl chloride. The colloidal palladium activation solution deposits a thin layer of metallic palladium over the plastic surface.[10] The metallic palladium induces the deposition of copper or nickel, which will not deposit directly onto plastic. The electroless nickel and copper plate are applied to impart electrical conductivity to the part; otherwise, the insulating surface of the plastic could not be electroplated with chromium. The electroless nickel plating or copper electroplating baths develop a film on the plastic about 1.0 micrometer (μm) (3.9×10^{-5} inch [in.]) thick. The plating time for electroless nickel

TABLE 2. TYPICAL OPERATING PARAMETERS FOR DECORATIVE CHROMIUM PLATING

Plating thickness, μm (mil)	0.003-2.5 (0.0001-0.1)
Plating time, min	0.5-5
Chromic acid concentration, g/ℓ (oz/gal)	225-375 (30-50)
Temperature of solution, °C (°F)	38-46 (100-115)
Voltage, volts	a
Current, A	b
Current density, A/m^2 $(A/ft^2)^c$	540-2,400 (50-220)

[a]Depends on the distance between the anodes and the items being plated.
[b]Depends on the amount of surface area being plated.
[c]Amperes per square meter (square foot) of surface area plated.

TABLE 3. CHROMIC ACID/SULFURIC ACID ETCH SOLUTION

Concentrated sulfuric acid, g/ℓ (oz/gal)	172 (23)
Chromic acid, g/ℓ (oz/gal)	430 (57)
Temperature, °C (°F)	60-65 (140-149)
Immersion time, min	3-10

plating and electroless copper plating ranges from 10 to 15 minutes and 15 to 30 minutes, respectively, at temperatures ranging from 25° to 35°C (77° to 95°F). The components of the plating baths include the metal salt (nickel or copper), a reducing agent, a complexing agent, a stabilizer, and a pH buffer system.[11] The electroplating of plastics follows the same cycle as that described for decorative chromium electroplating.[12]

3.1.1.4 Chromic Acid Anodizing. Chromic acid anodizing is used primarily on aircraft parts and architectural structures that are subject to high stress and corrosion. Chromic acid anodizing is used to provide an oxide layer on aluminum that imparts the following properties:

1. Corrosion protection;
2. Electrical insulation;
3. Ease of coloring; and
4. Improved dielectric strength.[13]

Figure 1 presents a flow diagram for a typical chromic acid anodizing process.

There are four primary differences between the equipment used for chromium electroplating and that used for chromic acid anodizing: (a) chromic acid anodizing requires the rectifier to be fitted with a rheostat or other control mechanism to permit starting at about 5 V, (b) the tank is the cathode in the electrical circuit, (c) the aluminum substrate acts as the anode, and (d) sidewall shields typically are used instead of a liner in the tank to minimize short circuits and to decrease the effective cathode area.[14] Types of shield materials used are herculite glass, wire safety glass, neoprene, and vinyl chloride polymers.[15]

The following pretreatment steps typically are used to clean the aluminum before anodizing:

1. Alkaline soak;
2. Desmut;
3. Etching; and
4. Vapor degreasing.

The pretreatment steps used for a particular aluminum substrate depend upon the amount of smut and the composition of the aluminum. The aluminum substrate is rinsed between pretreatment steps to remove cleaners.

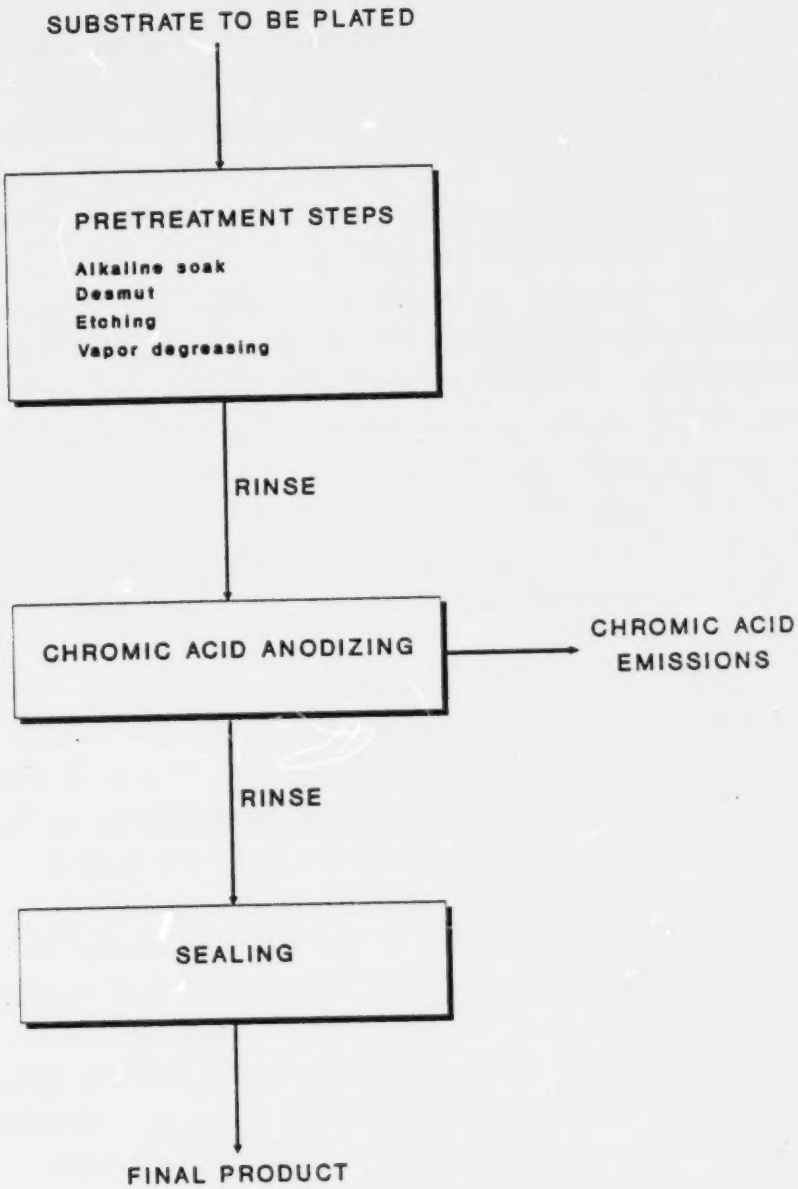


Figure 1. Flow diagram for a typical chromic acid anodizing process.

The alkaline soak is the primary preparatory step in cleaning the aluminum; its purpose is to dislodge soil from the aluminum surface. The solutions for alkaline cleaning are typically made up of compounds such as sodium carbonate, sodium phosphate, and sodium hydroxide and usually contain a small amount of silicate to prevent metal attack.[16] The alkaline soak consists of immersing the metal in the alkaline solution that is mildly agitated with air.

The purpose of desmutting is to remove soil or grease films that cleaners and etchants leave behind. Desmutting baths typically consist of a cold nitric acid solution mixed with water at a concentration ranging from 5 to 50 percent acid by volume. The nitric acid bath also is used either as a bleaching treatment to remove dyes from faulty coatings or as part of the technique of producing multicolor coatings.[17] Other desmutting treatments use combinations of chromic, phosphoric, and sulfuric acids depending upon the amount of smut to be removed or the aluminum composition.

When a dull finish is desired, the aluminum is etched before anodizing. Etching baths consist of a dilute solution of soda ash, caustic soda, or nitric acid.[18] The degree of etching desired and the composition of the aluminum being treated determine the concentration of the etch solution, temperature of the bath, and duration of the etch.

The vapor degreasing step removes any residual oil or grease on the surface of the aluminum prior to the anodizing operation.

Typical operating parameters for chromic acid anodizing baths are presented in Table 4.[19,20] The voltage is applied step-wise (5 V per minute) from 0 to 40 V and maintained at 40 V for the remainder of the anodizing time. A low starting voltage (i.e., 5 V) minimizes current surge that may cause "burning" at contact points between the rack and the aluminum part. The process is effective over a wide range of voltages, temperatures, and anodizing times. All other factors being equal, high voltages tend to produce bright transparent films, and lower voltages tend to produce opaque films.[21] Raising the bath temperature increases current density to produce thicker films in a given time period. Temperatures up to 49°C (120°F) typically are used to produce films that are to be colored by dyeing.[22] The amount of current varies depending on the size of the

TABLE 4. TYPICAL OPERATING PARAMETERS FOR CHROMIC ACID ANODIZING

Chromic acid concentration, g/ℓ (oz/gal)	50-100 (6.67-13.3)
Temperature, °C (°F)	32-35 (90-95)
Plating time, min	30-60
pH	0.5-0.85
Current density, A/m^2 (A/ft^2)[a]	1,550-7,750 (144-720)
Voltage (step-wise), volts	30-40
Film thickness, μm (mil)	0.5-1.27 (0.02-0.05)

[a]Amperes per square meter (square foot) of surface area plated.

aluminum parts; however, the current density typically ranges from 1,550 to 7,750 A/m^2 (144 to 720 A/ft^2).

The postanodizing steps include sealing and air drying. Sealing causes hydration of the aluminum oxide and fills the pores in the aluminum surface. As a result, the elasticity of the oxide film increases, but the hardness and wear resistance decrease.[23] Sealing is performed by immersing aluminum in a water bath at 88° to 99°C (190° to 210°F) for a minimum of 15 minutes.[24] Chromic acid or other chromates may be added to the solution to help improve corrosion resistance. The aluminum is allowed to air dry after it is sealed.

3.1.1.5 Trivalent Chromium Plating. Trivalent chromium electroplating baths have been developed primarily to replace decorative hexavalent chromium plating baths. Development of a trivalent bath has proven to be difficult because trivalent chromium solvates in water to form complex stable ions that do not readily release chromium. The trivalent chromium baths that have been developed are proprietary baths.

There are two types of trivalent chromium processes on the market: single-cell and double-cell. The major differences in the two processes are that (1) the double-cell process solution contains minimal-to-no chlorides whereas the single-cell process solution contains a high concentration of chlorides; and (2) the double-cell process utilizes lead anodes that are placed in anode boxes that contain a dilute sulfuric acid solution and are lined with a permeable membrane whereas the single-cell process utilizes carbon or graphite anodes that are placed in direct contact with the plating solution.[25]

The advantages of the trivalent chromium processes over the hexavalent chromium process are (1) fewer environmental concerns, (2) higher productivity, and (3) lower operating costs. In the trivalent chromium process, hexavalent chromium is a plating bath contaminant. Therefore, the bath does not contain any appreciable amount of hexavalent chromium, which is more toxic than trivalent chromium. The total chromium concentration of trivalent chromium solutions is approximately one-fifth that of hexavalent chromium solutions.[26] As a result of the chemistry of the trivalent chromium electrolyte, misting does not occur during plating, as it does during hexavalent chromium plating. Use of trivalent chromium

also reduces waste disposal problems and costs. Waste treatment of hexavalent chromium is a two-stage process. The hexavalent chromium is first reduced to the trivalent chromium ion; then it can be precipitated as chromium hydroxide. Trivalent chromium plating solution wastewaters are already in the reduced trivalent state and require only the chromium hydroxide precipitation step.

Productivity is increased when trivalent chromium processes are used because less stripping and replating of parts are required, more parts can be placed on a rack, and more racks can be placed on a workbar.[27]

The cost of operating a trivalent chromium process is less than that of a hexavalent chromium process because of the lower wastewater treatment costs and lower operating costs due to a reduction in rejects and high productivity.

The disadvantages of the trivalent chromium process are that the process is more sensitive to contamination than the hexavalent chromium process and the trivalent chromium process cannot plate the full range of plate thicknesses that the hexavalent chromium process can.[28] Because it is sensitive to contamination, the trivalent chromium process requires more thorough rinsing and tighter laboratory control than the hexavalent chromium process. Trivalent chromium baths can plate thicknesses ranging up to 0.13 to 25 micrometers (μm) (0.005 to 1.0 mils).[28] The hexavalent chromium process can plate thicknesses up to 762 μm (30 mils). Therefore, trivalent chromium solutions cannot be used for most hard chromium plating applications.

The plating efficiency of a trivalent chromium bath, approximately 20 to 25 percent, is slightly higher than that of a hexavalent chromium plating bath.[29] The color, hardness, and corrosion resistance of trivalent chromium deposits are comparable to those of hexavalent chromium deposits.[30] However, the composition of the trivalent chromium deposit is significantly different than that of the hexavalent chromium deposit. Table 5 presents the composition of trivalent and hexavalent chromium deposits.[31]

TABLE 5. HEXAVALENT AND TRIVALENT CHROMIUM DEPOSIT COMPOSITIONS

Chromium deposit	Carbon, % wt	Oxygen, % wt	Chromium, % wt
Hexavalent	0.0	0.4	99+
Trivalent	2.9	1.6	95+

3.1.2 Uncontrolled Chromium Emissions

Emissions of chromic acid mist from the electrodeposition of chromium from chromic acid plating baths occur because of the inefficiency of the hexavalent chromium plating process; only about 10 to 20 percent of the current applied actually is used to deposit chromium on the item plated. Eighty to ninety percent of the current applied is consumed by the evolution of hydrogen gas at the cathode with the resultant liberation of gas bubbles. Additional bubbles are formed at the anode due to the evolution of oxygen. As the bubbles burst at the surface of the plating solution, a fine mist of chromic acid droplets is formed.

3.1.2.1 Hard Chromium and Decorative Electroplating Operations. Uncontrolled emission data for 10 hard chromium plating operations and 2 decorative chromium plating operations are presented in Table 6. These data were obtained from 11 EPA tests and 1 non-EPA test. Table 7 presents tank parameters and process operating parameters monitored during each of the 12 tests. The process parameters monitored during testing include current supplied to the plating baths, voltage, chromic acid concentration, and temperature of the plating baths. The chromic acid concentration and temperature did not vary significantly within each type operation for the emission tests and appeared to be representative of typical operating values for conventional hard and decorative chromium plating operations. The amount of current supplied during testing varied considerably because of the different types and quantities of parts plated.

Based on the existing test data, an uncontrolled emission factor of 10 milligrams of hexavalent chromium per ampere-hour (mg/Ah) (0.15 grain per ampere-hour [gr/Ah]) is considered to be representative of uncontrolled emissions from a hard chromium electroplating operation, and an uncontrolled hexavalent chromium emission factor of 2 mg/Ah (0.03 gr/Ah) is considered representative of uncontrolled emissions from a decorative chromium electroplating operation.

The emission factor for uncontrolled chromium emissions from decorative chromium plating operations is based on EPA-approved test data from two plants whose tanks represent the extremes in tank size for decorative chromium plating. Although the sizes of these tanks may not be

TABLE 6. UNCONTROLLED EMISSION DATA FOR TOTAL AND HEXAVALENT CHROMIUM FROM CHROMIUM PLATING OPERATIONS[a]

Plant	Process conditions: No. of tanks	Process conditions: Total tank surface area, m^2 (ft^2)	Process conditions: Ampere-hours	Actual gas flow rate, m^3/min (ft^3/min)	Mass emission rate, kg/h (lb/h): Total Cr	Mass emission rate, kg/h (lb/h): Cr^{+6}	Process Cr^{+6} emission rate, mg/A•h (gr/A•h)
Hard chromium plating							
Plant A[b,32]	1	5.8 (63)	14,000	226 (7,970)	0.029 (0.064)	0.026 (0.057)	4.0 (0.06)
Plant B[c,33]	2	2.5 (27)	14,400	152 (5,390)	0.008 (0.018)	0.015 (0.033)	3.2 (0.05)
Plant C[d,34]	4	8.4 (90)	20,000	339 (12,000)	e	0.039 (0.085)	4.6 (0.07)
Plant D[c,35]	1	5.2 (56)	19,800	177 (6,260)	0.076 (0.167)	0.076 (0.168)	9.1 (0.14)
Plant E[c,36]	1	3.4 (37)	11,700	190 (6,670)	e	0.031 (0.069)	6.3 (0.10)
Plant F[f,37]	1	1.8 (20)	12,200	128 (4,540)	e	0.083 (0.183)	16.3 (0.25)
Plant G[c,38]	1	1.4 (1.5)	8,900	95 (3,360)	e	0.024 (0.053)	6.5 (0.10)
Plant H[c,39]	1	5.5 (60)	3,440	242 (8,540)	0.009 (0.019)	g g	3.6 (0.06)[h]
Plant I[i,40]	2	9.0 (99)	8,530	290 (10,300)	0.100 (0.221)	0.090 (0.199)	22.5 (0.35)
Plant J[c,41]	3	6.6 (71)	8,790	512 (18,100)	0.044 (0.097)	0.046 (0.102)	15.5 (0.24)
Average							9.8 (0.15)

(continued)

TABLE 6. (continued)

Plant	Process conditions: No. of tanks	Process conditions: Total tank surface area, m^2 (ft^2)	Process conditions: Ampere-hours	Actual gas flow rate, m^3/min (ft^3/min)	Mass emission rate, kg/h (lb/h): Total Cr	Mass emission rate, kg/h (lb/h): Cr^{+6}	Process Cr^{+6} emission rate, mg/A•h (gr/A•h)
Decorative chromium plating							
Plant K[c,42]	1	22.6 (240)	97,000	683 (24,100)	e	0.066 (0.145)	2.0 (0.03)
Plant L[c,43]	1	2.9 (30.8)	6,500	70 (2,470)	e	0.004 (0.008)	1.3 (0.02)
Average							1.6 (0.02)

[a] All tests were performed by EPA except for the Plant H test which was performed by the Naval Energy and Environmental Support Activity, Port Hueneme, California.
[b] Ampere-hour and mass emission rate values are based on an average of four test runs.
[c] Ampere-hour and mass emission rate values are based on an average of three test runs.
[d] Ampere-hour and mass emission rate values are based on an average of six test runs.
[e] Total chromium emissions were not determined.
[f] Ampere-hour and mass emission rate values are based on an average of five test runs.
[g] Hexavalent chromium emissions were not reported.
[h] Not included in average value because data are based on total chromium.
[i] Ampere-hour and mass emission rate values are based on an average of 11 test runs.

TABLE 7. TANK PARAMETERS AND PROCESS OPERATING PARAMETERS MONITORED DURING CHROMIUM PLATING TESTS

Plant	Tank parameters			Average process parameters monitored			
	No. of tank(s)	Total tank surface area, m^2 (ft^2),[a]	Total tank capacity, ℓ (gal)[b]	Current, amperes	Voltage, volts	Chromic acid concentration, g/ℓ (oz/gal)	Bath temp., °C (°F)
Hard chromium plating							
Plant A[32]	1	5.8 (63)	10,710 (2,830)	6,220	9.0	254 (34)	52 (125)
Plant B[33]	2	2.5 (27)	4,130 (1,090)	1,610	12.3	208 (28)	62 (145)
Plant C[34]	4	8.4 (90)	35,000 (9,250)	2,860	7.9	250 (33)	54 (130)
Plant D[35]	1	5.2 (56)	15,820 (4,180)	8,390	7.4	156 (21)	52 (125)
Plant E[36]	1	3.4 (37)	9,270 (2,450)	4,970	7.0	250 (33)	54 (130)
Plant F[37]	1	1.8 (20)	4,810 (1,270)	2,640	4.9	210 (28)	56 (133)
Plant G[38]	1	1.4 (15)	5,720 (1,510)	3,480	4.9	210 (28)	55 (131)
Plant H[39]	1	5.5 (60)	7,190 (1,900)	2,480	6.6	210 (28)	60 (140)
Plant I[40]	2	9.0 (99)	11,210 (2,960)	1,140	7.7	225 (30)	59 (138)
Plant J[41]	3	6.6 (71)	6,090 (1,610)	1,150	6.1	173 (23)	49 (120)
Decorative chromium plating							
Plant K[42]	1	22.6 (240)	61,170 (16,160)	21,320	22.4	300 (40)	54 (130)
Plant L[43]	1	2.9 (31)	3,860 (1,020)	2,700	5.1	241 (32)	48 (119)

[a] m^2 = square meters, ft^2 = square feet.
[b] ℓ = liters, gal = gallons.

typical of the sizes of other decorative plating tanks, there is insufficient evidence to show that emissions are directly proportional to tank size. In any case, the uncontrolled emissions have been normalized to account for tank size using the ampere-hours term in the emission factor. Because the data are limited, a conservative approach was taken in selecting the emission factor for decorative plating. Thus, a value of 2 mg/Ah was selected instead of the average value for the two tests.

3.1.2.2 Chromic Acid Anodizing Operations. Uncontrolled emission data for chromic acid anodizing operations were not obtained through an EPA source test at an anodizing facility. Instead, an estimate of the amount of hexavalent chromium emissions was made by performing a mass balance on a scrubber used to control emissions from a chromic acid anodizing operation. Outlet scrubber water grab samples were analyzed to determine the amount of hexavalent chromium in the sample, and a mass balance was performed on the scrubber to determine the inlet hexavalent chromium emission rate. The results of this mass balance indicate that **an uncontrolled of emission factor of 6.0×10^{-4} kilogram of hexavalent chromium per hour per square meter of tank surface area (1.2×10^{-4} pound per hour per square foot of tank surface area) is appropriate to characterize emissions from chromic acid anodizing.**[44] Alternatively, if the tank surface area is unknown, uncontrolled emission rates can be used to approximate the level of uncontrolled chromium emissions. The results of the mass balance at the small anodizing operation (tank capacity ~1,900 liters [500 gallons]) and results from a non-EPA emission test at a large chromic acid anodizing operation (tank capacity ~17,600 liters [4,600 gallons]) indicate uncontrolled emission rates range from 0.0012 to 0.0028 kg/h (0.0026 to 0.0062 lb/h), respectively.[44] At this time, there are insufficient data from anodizing operations to determine conclusively that one emission factor format is more appropriate than the other.

3.1.3 Emission Reduction Techniques

The principal techniques used to control emissions of chromic acid mist from decorative and hard chromium plating and chromic acid anodizing operations include add-on control devices and chemical fume suppressants. The control devices most frequently used are mist eliminators and wet scrubbers that are operated at relatively low pressure

drops. Because of the corrosive properties of chromic acid, control devices typically are made of polyvinyl chloride (PVC) or fiberglass.

Chemical fume suppressants are added to decorative chromium plating and chromic acid anodizing baths to reduce chromic acid mist. Although chemical agents alone are effective control techniques, many plants use them in conjunction with a control device.

Chevron-blade and mesh-pad mist eliminators are the types of mist eliminators most frequently used to control chromic acid mist. The most important mechanism by which mist eliminators remove chromic acid droplets from gas streams is the inertial impaction of droplets onto a stationary set of blades or a mesh pad. Mist eliminators typically are operated as dry units that are periodically washed down with water to clean the impaction media.

The wet scrubbers typically used to control emissions of chromic acid mist from chromium plating and chromic acid anodizing operations are single and double packed-bed scrubbers. Other scrubber types used less frequently include fan-separator packed-bed and centrifugal-flow scrubbers. Scrubbers remove chromic acid droplets from the gas stream by humidifying the gas stream to increase the mass of the droplet particles, which are then removed by impingement on a packed bed. Once-through water or recirculated water typically is used as the scrubbing liquid because chromic acid is highly soluble in water.

Chemical fume suppressants are surface-active compounds that are added directly to chromium plating and chromic acid anodizing baths to reduce or control misting. Fume suppressants are classified as temporary or as permanent. Temporary fume suppressants are depleted mainly by the decomposition of the fume suppressant and dragout of the plating solution, and permanent fume suppressant are depleted mainly by dragout of the plating solution. Fume suppressants, which are manufactured in liquid, powder, or tablet form, include wetting agents that reduce misting by lowering the surface tension of the plating or anodizing bath, foam blankets that entrap chromic acid mist at the surface of the plating solution, or combinations of both a wetting agent and foam blanket.

The performance capabilities of the control devices used to control chromic acid mist are presented in Table 8. The air pollution control devices tested include four mist eliminators, three packed-bed scrubbers, and one packed-bed scrubber in conjunction with a mist eliminator used to control emissions from hard chromium plating operations. In addition, one emission test was conducted at a decorative chromium plating facility to determine the performance of chemical fume suppressants in controlling chromic acid mist.

The average hexavalent chromium removal efficiency of mist eliminators was 98 percent for mist eliminators with double sets of blades, 90 percent for mist eliminators with single sets of blades, and 98 percent for mesh pad units. The average hexavalant chromium removal efficiency of scrubbers was 98 percent. The hexavalant chromium removal efficiency of the scrubber in conjunction with the mist eliminator was 95 percent.

For decorative chromium plating operations, the performance efficiency of both chemical fume suppressants tested (a foam blanket and a combination of a foam blanket and wetting agent) was greater than 99 percent. This performance efficiency is achievable as long as vendor recommendations on the makeup and use of the fume suppressants are followed rigorously.

3.1.4 Nationwide Emission Estimates

Table 9 presents the estimated number of operations and the nationwide annual emission rate for each type of operation. The assumptions regarding the existing control levels for each type operation were derived from data obtained during the development of the NESHAP for chromium electroplating operations. The nationwide emission rate for hard chromium electroplating operations was based on the assumption that 30 percent of operations are uncontrolled, 30 percent of operations are controlled by mist eliminators with single sets of blades (90 percent efficient), and 40 percent are controlled by single packed-bed scrubbers (97 percent efficient). The nationwide emission rate for decorative chromium electroplating operations was based on the assumption that 15 percent of operations are uncontrolled, 80 percent are controlled by chemical fume suppressants (97 percent efficient), and 5 percent are

TABLE 8. PERFORMANCE LEVELS OF INDIVIDUAL CONTROL DEVICES

Plant code	Plant name	Description of control device	No. of runs averaged	Concentration, mg/dscm		Mass emission rate, kg/h		Efficiency, percent[a]	Process emission rate, mg/Ah	
				Inlet	Outlet	Inlet	Outlet		Inlet	Outlet
HARD CHROMIUM PLATING										
Chevron-blade mist eliminators										
A		Single set of overlapping type blades	4	2.030	0.306	0.0260	0.0033	87.9	3.96	0.55
B		Single set of overlapping type blades	3	1.760	0.149	0.0151	0.0013	91.3	3.16	0.27
D		Double set of overlapping type blades	3	7.690	0.124	0.0763	0.0012	98.4	9.06	0.15
Mesh-pad mist eliminators										
F		Two mesh pads in series	5	11.400	0.0326	0.0829	0.0002	99.7	16.3	0.04
G		Two mesh pads in series	3	4.410	0.0435	0.0241	0.0003	98.9	6.52	0.07
H[b]		One mesh pad	3	0.609	0.0257	0.0087	0.0005	94.5	3.60	0.18
E[c]		Two sets of chevron-blades followed by two mesh pads	3	3.070	0.040	0.0313	0.0004	98.7	6.33	0.08
Packed-bed scrubbers										
I		Single packed-bed scrubber	11	5.510	0.0302	0.0900	0.0005	99.4	22.5	0.14
J		Double packed-bed scrubber	3	1.670	0.0523	0.0464	0.0015	96.2	15.5	0.56
C		Double packed-bed scrubber followed by chevron-blade mist eliminator with a double set of wave-type blades	6	2.040	0.081	0.0388	0.0015	95.4[d]	4.57	0.14
DECORATIVE CHROMIUM PLATING										
Fume suppressants										
L		1. Foam blanket	3	0.916	0.0041	0.0036	0.00002	+99.5	1.34	0.006
		2. Foam blanket in combination with wetting agent	3	0.916	0.0021	0.0036	0.00001	+99.8	1.34	0.003

[a]Efficiencies are based on the average of efficiencies from each run. Therefore, they may not agree with the values obtained by calculating the efficiency from the average inlet and outlet rate.
[b]Results are for total chromium. Hexavalent chromium analyses were not performed.
[c]A moisture extractor preceded the mist eliminator unit. However, the emission data for the combined control techniques were attributed to the mist eliminator unit only. Any droplets caught by the moisture extractor would have been collected by the mist eliminator unit, if the moisture extractor was eliminated from the system.
[d]The efficiency presented is the combined efficiency of both units.

TABLE 9. NATIONWIDE NUMBER OF OPERATIONS AND ESTIMATED HEXAVALENT CHROMIUM EMISSIONS FROM CHROMIUM ELECTROPLATING AND CHROMIC ACID ANODIZING OPERATIONS

Operation	No. of plants nationwide	Nationwide Cr^{+6} emissions, Mg/yr (tons/yr)
Hard chromium plating[1]	1,540	145 (160)
Decorative chromium plating[1]	2,800	10 (11)
Chromic acid anodizing[2]	680	3.6 (3.9)

controlled by single packed-bed scrubbers (95 percent efficient). The nationwide annual emission rate for chromic acid anodizing operations was based on the assumption that 40 percent of operations are uncontrolled, 10 percent are controlled by mist eliminators with single sets of blades (90 percent efficient), 30 percent are controlled by chemical fume suppressants (97 percent efficient), and 20 percent are controlled by single packed-bed scrubbers (95 percent efficient).

3.2 COOLING TOWERS

3.2.1 Background Information

Cooling towers are devices that cool warm water by contacting it with ambient air that is drawn or forced through the tower. This cool water is used to remove heat from a process or an HVAC chiller and is then recirculated to the cooling tower. Chemicals are added to this recirculating water to inhibit heat exchanger corrosion. One of the many classes of corrosion inhibitors used is chromium based. Air emissions of chromium occur when water droplets (and the chemicals they contain) entrained in the air stream that is drawn through the tower are emitted to the atmosphere. These droplet emissions are referred to as "drift." All cooling towers that are used to remove heat from an industrial process or chemical reaction are referred to as industrial process cooling towers (IPCT's). Towers that are used to cool heating, ventilation, and air conditioning (HVAC) and refrigeration systems are referred to as comfort cooling towers (CCT's).

3.2.1.1 Industrial Process Cooling Towers. Major users of IPCT's that also use chromium-based water treatment chemicals are chemical manufacturing plants, petroleum refineries, and primary metals facilities. Several miscellaneous manufacturing industries (textiles, tobacco products, tire and rubber products, and glass products) and utilities use chromium-based water treatment chemicals to a lesser degree. It is estimated that IPCT's are used at approximately 190 petroleum refineries, 1,800 chemical manufacturing plants, 240 primary metals plants, and 730 plants in the miscellaneous industries.[45] In addition, the percentage of cooling towers using chromium-based water treatment chemicals in each industry is estimated as 70 percent at petroleum refineries, 40 percent at chemical manufacturing plants, 20 percent at

primary metals facilities, 15 percent at plants in the tire and rubber industry, and 5 percent at plants in the other miscellaneous industries.[45] In the utilities industry, it was reported that chromium-based water treatment chemicals are used at two electric power plants.[46] When combined with data from plant responses to EPA information requests in each of these industries, these estimates result in a total of about 2,855 IPCT's using chromium-based water treatment chemicals: 476 at petroleum refineries, 2,039 at chemical plants, 224 at primary metals plants, 110 at miscellaneous plants, and 6 at utilities. The nationwide baseline Cr^{+6} emissions from these towers are estimated to be 85 megagrams per year (Mg/yr) (94 tons per year [tons/yr]).[45]

3.2.1.2 Comfort Cooling Towers. Comfort cooling towers are used in all States in the U.S., primarily in urban areas. Major users of CCT's with HVAC systems include hospitals, hotels, educational facilities, office buildings, and shopping malls. Refrigeration systems that may operate with CCT's include ice skating rinks, cold storage (food) warehouses, and other commercial operations. The EPA estimates that the nationwide population of CCT's is 250,000 units and that 15 percent of CCT's (about 37,500) use chromium-based water treatment chemicals. These CCT's are estimated to emit between 7.2 and 206 Mg/yr (8 to 227 tons/yr) of chromium.[47] Chromium use in CCT's appears to be distributed randomly across the country.[47]

In the preparation of the proposed rule for CCT's under the Toxic Substances Control Act (TSCA) (see 52 FR 10206), EPA developed model tower parameters and estimates of chromium emissions per model tower to represent the population of CCT's in the U.S. Table 10 presents the model parameters and baseline (i.e., low efficiency drift eliminator [LEDE]) emission estimates.[47]

The emission estimates in Table 10 are based on an emission factor developed from EPA- and industry-sponsored cooling tower emission tests. Because the emission factors developed to estimate Cr^{+6} emissions from cooling towers are independent of tower operating parameters (recirculation rate, chromate concentration, cooling range), the factors are applicable to both CCT's and IPCT's. Section 3.2.3.1 of this document discusses specific emission factors to use for estimating Cr^{+6} emissions from cooling towers on a case-by-case basis. [Note: The proposed TSCA rule

TABLE 10. MODEL COMFORT COOLING TOWERS AND HOURLY BASELINE Cr^{+6} EMISSIONS

Model tower	Model building size, m^2 (ft^2)	Model tower cooling requirements W (Btu/h)	Tons	Flow rates, ℓ/min (gal/min) Recirculation rate	Evaporation rate	Blowdown rate	Chromium emissions per tower, mg/h (lb/1,000 h)
1	673 (7,240)	95,400 (325,800)	27	246 (65)	2.08 (0.55)	0.53 (0.14)	19.9 (0.044)
2	1,460 (15,720)	207,100 (707,400)	59	534 (141)	4.54 (1.20)	1.14 (0.30)	43.2 (0.095)
3	3,405 (36,650)	482,900 (1,649,000)	137	1,250 (330)	10.6 (2.80)	2.65 (0.70)	101 (0.222)
4	6,224 (66,990)	882,900 (3,015,000)	251	2,280 (602)	19.4 (5.12)	4.85 (1.28)	184 (0.406)
5	12,338 (132,800)	1,750,000 (5,976,000)	498	4,520 (1,194)	38.4 (10.15)	9.61 (2.54)	365 (0.804)
6	37,626 (405,000)	5,338,000 (18,230,000)	1,520	13,800 (3,642)	117.0 (30.96)	29.3 (7.74)	1,110 (2.45)

Assumptions:

Wet bulb temperature = 23.9°C (75°F)
Hot water temperature = 29.4°C (85°F)
Cooling range = 5.6°C (10°F)
Cooling requirements = 142 W/m^2 floorspace (45 $Btu/ft^2/h$)
Cycles of concentration = 5
Latent heat/total heat = 0.8
Chromate concentration = 10 ppm
Chromium emission factor = 0.0003 mg Cr^{+6}/(ppm Cr^{+6})(liter H_2O)
(2.504×10^{-9} lb Cr^{+6}/ppm Cr^{+6}/gal H_2O)

would prohibit the use of chromium-based chemicals in CCT's. If promulgated, this rule would have the effect of reducing Cr^{+6} emissions from CCT's to zero.]

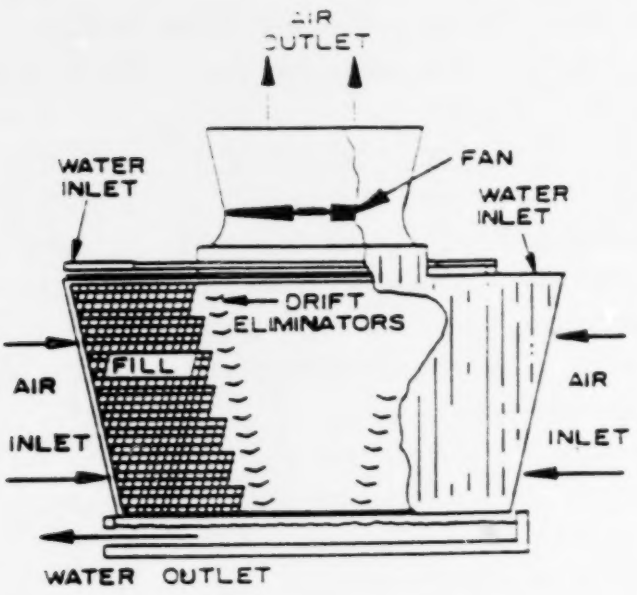
3.2.1.3 Cooling Tower Fundamentals. Schematics of typical cooling tower designs are shown in Figure 2.[48] The major cooling tower components include the fan(s), fill material, water distribution deck or header, drift eliminator, structural frame, and cold water basin. Other components that affect tower operation include the pumps and pipes necessary to circulate the cooling water through the cooling tower and heat exchanger loops.

Most IPCT's are designed with induced-draft airflow, but many have forced-draft airflow, and some (especially in the utilities industry) have natural-draft airflow. Induced draft is provided by a propeller-type axial fan located in the stack at the top of the tower. Forced-draft towers are usually smaller than induced-draft towers and have either centrifugal fans located at the base of the tower, which is constructed as a plenum to provide positive-pressure airflow through the fill material, or axial fans located on the side of the tower. Natural-draft airflow relies on air currents created by temperature differences between the air in the tower and the atmosphere. When the cooling demands are minimal and the air temperature is low enough, water can be circulated through the tower and cooled sufficiently without using the fans. In these instances, a natural draft is created in the cooling tower.

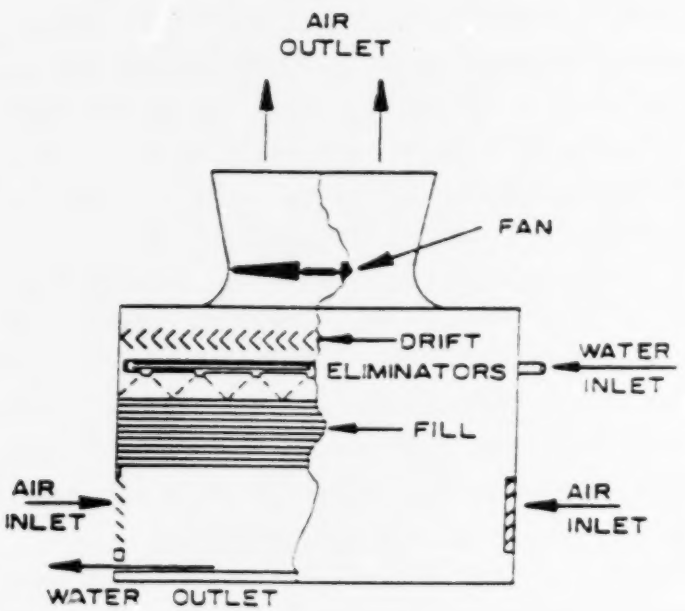
The direction of the airflow through a mechanical draft tower is either crossflow or counterflow. Crossflow refers to horizontal airflow through the fill, and counterflow refers to upward vertical airflow. Fill material is used to maintain an even distribution of water across the horizontal plane of the tower and to create as much water surface as practical to enhance evaporation and sensible heat transfer.

3.2.2 Potential Emission Reduction Techniques

Techniques to control chromium emissions from cooling towers involve two different strategies: modification of chromium addition to the recirculating water, and improved reduction of drift. The first technique involves reducing the concentration of chromium in the water treatment program, thereby reducing the concentration of chromium in the drift



MECHANICAL DRAFT
CROSS-FLOW TOWER



MECHANICAL DRAFT
COUNTER-FLOW TOWER

Figure 2. Internals of crossflow and counterflow cooling towers (reprinted from Reference No. 48).

emitted. The second technique involves retrofitting towers that normally have LEDE's with high-efficiency drift eliminators (HEDE's) to reduce drift emissions to the lowest possible rate.

3.2.2.1 Alternative Water Treatment Programs. Responses to 28 EPA information requests and a survey of the Chemical Manufacturers Association indicate that the average chromate concentration for those IPCT's using chromium-based corrosion inhibitors is 13 ppm.[45,49] One potential chromium emission reduction technique involves alternative water treatment programs such as programs with lower chromate levels or nonchromate treatments.

A low-chromate treatment program would reduce Cr^{+6} emissions from IPCT's by limiting the chromate concentration in cooling water. Water treatment programs are available that maintain average chromate concentrations of 0.5 to 4 ppm in the recirculating water, but these programs have not always been successful in industrial applications. Low-chromate programs that have provided acceptable results in a number of cases maintain chromate concentrations in the range of 4 to 6 ppm.

Because of National Pollution Discharge Elimination System (NPDES) chromium restrictions and other regulations, nonchromium treatments are now more widely used than chromium treatments. The most common nonchromium treatment program is phosphate based, but others include molybdates, zinc, and all-organic treatments (primarily organo-phosphorus compounds). However, these alternative programs may not perform corrosion inhibition functions as well or as cheaply as chromates depending on the individual cooling tower system. The performance of any treatment program is dependent on water quality parameters (pH, alkalinity, hardness, and conductivity) and operating conditions (water temperature, flow velocity, inhibitor concentration, and the presence of contaminants such as H_2S, SO_2, NH_3, and NO_2) that are specific to each cooling system.

3.2.2.2 Low- and High-Efficiency Drift Eliminators. Water droplets entrained in the air and the dissolved and suspended solids contained in the droplets that are emitted from cooling towers are referred to as drift. Drift eliminators can be installed at the exit of the fill sections to reduce the amount of drift in the exiting airflow. Historically, the purpose of drift reduction has been to alleviate the

nuisance deposition of water drift and its dissolved solids on nearby buildings or on personal property such as automobiles. More recently, the concern has focused on the environmental impact caused by the compounds contained in the drift and, thus, on the deposition of these compounds. Drift eliminators are designed with pressure drops lower than those of other air pollution control equipment and rely primarily upon the impaction of water droplets on drift eliminator surfaces to reduce the concentration of drift from the exit air of cooling towers. The drift eliminator blades are configured to force directional changes in the airflow such that the momentum of the water droplets causes them to impinge onto the blade surfaces. The number of directional airflow changes, the spacing between the blade surfaces, the angle of directional change, and the capability to return the collected water to a quiescent area of the plenum are the major design features (parameters) in drift eliminators that affect efficiency. Drift eliminators are constructed of wood, PVC, metal, asbestos-cement, polystyrene, or cellulose. The material most often specified is PVC.

Figure 3 presents schematics of the three major drift eliminator designs: herringbone (blade-type), waveform, and cellular (or honeycomb). Low-efficiency drift eliminators include herringbone, some waveform (sinusoidal), and some cellular designs. Herringbone designs are constructed to create two or three major directional changes in the airflow. The blades are sloped in opposing directions in a manner that provides drainage of the accumulated drift into the fill area. The blades typically are constructed of wood, but other materials (e.g., metal and asbestos cement board) also are used. Waveform drift eliminators are configured in a sinusoidal wave pattern such that two major directional changes in the airflow are created. The sinusoidal blades are constructed of asbestos cement board or PVC material. Cellular drift eliminators are configured with thinner blades in a honeycomb pattern. The airflow passages in the cellular drift eliminators, which are narrower than passages in other designs, reduce the distance a droplet must travel across the stream to impact on the surface. Drainage of the collected water to prevent reentrainment is not a design criteria of LEDE's.

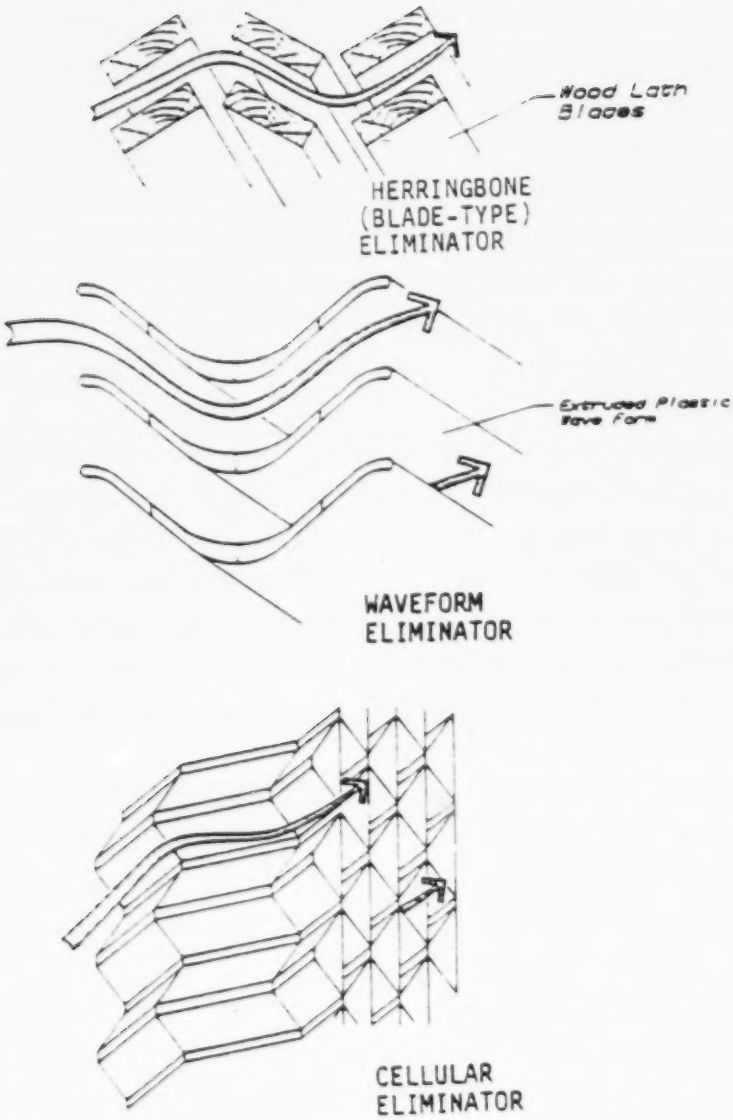


Figure 3. Designs of various drift eliminators (reprinted from Reference No. 50).

High-efficiency drift eliminators include a few of both cellular and sinusoidal designs. The cellular HEDE's that achieve the higher efficiencies are designed with complex configurations that contain numerous, closely constructed airflow passages. Thin materials of construction are used to reduce the area of blockage to the airflow and minimize the pressure drop that is created by the eliminator. For sinusoidal drift eliminators, the blades are placed closer together in high-efficiency designs than in low-efficiency designs, and the exit is configured with a tip for draining captured water that would otherwise be partially reentrained in the airflow. Typically, drainage of water into a quiescent area of the tower is a major design consideration of HEDE's. A few drift eliminators installed in towers built in recent years are more likely to be higher efficiency waveform or cellular units, but the vast majority of older towers still have lower efficiency herringbone and waveform eliminators.

The performance of a drift eliminator is affected primarily by the droplet or particle size and the airflow velocities through the drift eliminator. Small droplets are created both from evaporation of larger droplets and the physical breakage of larger droplets into small droplets. Parameters that affect the rate of evaporation and the size of droplets created include the water distribution system, the type of fill, the type of tower, the meteorological conditions, and the temperature of the recirculating water.

A drift eliminator manufacturer indicates that HEDE's can remove 80 to 90 percent or more of the drift discharged from low-efficiency herringbone drift eliminators.[50,51] These drift eliminator efficiencies, however, are based on data collected with a test method that has not been submitted to EPA for approval.

3.2.3 Cooling Tower Emissions

Three series of emission tests were conducted by EPA on IPCT's equipped with low- and high-efficiency drift eliminators. The results of these tests are presented in the next section.

3.2.3.1 Drift and Chromium Emissions. The drift rate (rate of water lost by entrainment in the cooling air drawn through the tower) is often expressed as the percentage of the recirculating water flow rate that is emitted. Likewise, the chromium emission rate can be expressed as a percentage of the recirculating chromium rate. However, the chromium emission rate from towers should not be confused with the drift rate. Based on test results, a drift eliminator manufacturer claims that the achievable drift rates range from 0.001 to 0.06 percent of the recirculating water. The approximate dividing line between drift rates for higher and lower efficiency drift eliminators is 0.008 percent. Those achieving a lower percentage are "higher efficiency," and those that cannot achieve 0.008 percent are "lower efficiency."[50-52]

Drift can be estimated by measuring the emission rate of an element (such as sodium, calcium, manganese, chromium, lithium or bromine) and assuming that the percentage of water emitted as drift is the same as the percentage of the recirculating element emitted. However, a claimed drift rate may or may not be equivalent to the element's emission rate depending on the way the drift rate was measured. Also, drift rate measurement results are highly dependent on the measurement method; therefore, achievable drift rate claims may not be comparable if they are based on different measurement methods.

The EPA-sponsored emission tests of IPCT's at three facilities used an isokinetic test method for chromium which is still under development. Emission factors relating the chromium emission rate to the chromium recirculation rate were developed from each of these emission tests. The average baseline (LEDE) and controlled (HEDE) emission factors for each test site are presented in Table 11. In addition, five industry-sponsored drift performance tests conducted by Midwest Research Institute and two chromium emission tests conducted by Mobil are included. The emission factors express the emission rate as a percentage of the recirculating rate (milligrams of chromium emitted per milligram of chromium recirculating in the tower multipled by 100). The most comprehensive emission tests were conducted at Plant B. At this plant, two towers of similar design located side-by-side were tested simultaneously under the same meteorological conditions. One tower was equipped with an LEDE and the other was equipped with an HEDE.

TABLE 11. EMISSION FACTORS FOR HEXAVALENT CHROMIUM FROM COOLING TOWERS[53-57]

Test site	Chromium emission factor, percent[a]	Standard deviation (percent relative standard deviation, percent)
EPA-sponsored tests		
A (HEDE)	0.0037 0.028 w/outliers	0.0020 (54) 0.035 w/outliers (126)
C (HEDE)	0.0038	0.0044 (116)
B (HEDE)	0.0087	0.0037 (43)
B (LEDE)	0.0267	0.0168 (63)
A (LEDE)	0.0318 0.141 w/outliers	0.0292 (92) 0.192 w/outliers (136)
Industry-sponsored tests		
MRI No. 3 (HEDE)	0.01	NA (--)
MRI No. 4 (HEDE)	0.007	NA (--)
Mobil-PTR Tower No. 5 (LEDE)	0.0334	0.0306 (92)
Mobil-North Tower No. 6 (LEDE)	0.0321	0.0156 (49)
MRI No. 1 (LEDE)	0.0305	NA (--)
MRI No. 2 (LEDE)	0.034	NA (--)
MRI No. 5/6 minerals test (LEDE)	0.018 0.021 w/outliers	0.0045 (25) 0.0094 w/outliers (45)

[a]Percentage of recirculating chromium that is emitted.

Since the completion of the emission tests at Plant B, additional methods development investigations have been conducted. These investigations have revealed that the chromium sampling method is subject to substantial error due to potentially severe problems associated with chromium recovery and cross-over contamination from sample run to sample run. The extent to which these problems appear in the test results obtained at Plants A, C, and Mobil is uncertain. As a result, the data presented in Table 11 should be used with caution.

The EPA believes that the tests at Plant B provide the best available data on the relative performance of HEDE's. **The EPA Method 13-type testing at Plant B indicated a Cr^{+6} emission factor of 0.03 percent of the recirculating Cr^{+6} for LEDE's and 0.0087 percent for HEDE's.** As discussed in Section 3.2.1.2, these factors can be used for both IPCT's and CCT's.

The current factors are based on the assumption that the ratio of hexavalent to total chromium in the emissions is the same as that in the cooling water. The test program conducted by the Agency has not conclusively identified the speciation of emissions (i.e., Cr^{+6} versus Cr^{+3}). For purposes of estimating Cr^{+6} emissions, the conservative assumption is that all of the chromium is Cr^{+6}.

3.2.3.2 Sample Calculation of Chromium Emissions. The chromium emission rate for any tower can be estimated by multiplying the emission factor by the recirculating rate of water and the chromium concentration in the recirculating water as shown in Equation (1).

$$E_{Cr} = K \cdot R \cdot C_{Cr} \quad (1)$$

where:

E_{Cr} = chromium emission rate, mg Cr/min

K = chromium emission factor, percent of recirculating chromium that is emitted

R = recirculating rate of cooling water, liters/min

C_{Cr} = concentration of chromium in the recirculating water, mg Cr/liter = ppm (multiply CrO_4 concentration by 0.448 to obtain Cr concentration)

For example, the following calculation estimates the emissions from a 10,000-gallon-per-minute (gal/min) IPCT with a recirculating chromate

concentration of 10 parts per million (ppm), equipped with a low-efficiency drift eliminator.

R = (10,000 gal/min)(3.785 liters/gallon) = 37,850 liters/minute

C_{Cr} = 10 ppm as CrO_4 = 4.48 ppm Cr

K = the emission factor for towers with low-efficiency drift eliminators; use K = 0.03 percent.

$E_{Cr} = K \cdot R \cdot C_{Cr}$ = (0.03%)(37,850)(4.48) = (0.0003)(37,850)(4.48) = 50.9 mg Cr emitted/min

To estimate the emissions from the same IPCT equipped with a high-efficiency drift eliminator, use K = 0.0087.

Therefore:

$E_{Cr} = K \cdot R \cdot C_{Cr}$ = (0.0087%)(37,850)(4.48) = (0.000087)(37,850)(4.48) = 14.8 mg Cr emitted/min

Thus, the emission reduction achieved by a HEDE compared to a LEDE is:

$$\frac{50.9-14.8}{50.9} \times 100 = 71 \text{ percent.}$$

The following example calculation estimates the emissions from a 500-gal/min CCT with a recirculating chromate concentration of 10 ppm, equipped with a low-efficiency drift eliminator.

R = (500 gal/min)(3.785 liters/gal) = 1,892.5 liters/min

C_{Cr} = 10 ppm as CrO_4 = 4.48 ppm Cr

K = 0.03 percent

$E_{Cr} = K \cdot R \cdot C_{Cr}$ = (0.03%)(1,892.5)(4.48) = (0.0003)(1,892.5)(4.48) = 2.5 mg Cr emitted/min

3.2.4 Nationwide Emissions Distribution by Industry

In developing the NESHAP for chromium emissions from IPCT's, EPA has generated industry-by-industry estimates of the total number of cooling towers, the number of towers using chromate treatments, and chromium emissions. Table 12 presents these estimates as currently known. The data show that the industries of greatest concern are chemical manufacturing (43 Mg/yr [47.5 tons/yr]), petroleum refining (31.8 Mg/yr [35.1 tons/yr]), and primary metals production (8.4 Mg/yr [9.3 tons/yr]).

Together, these industries represent 98.2 percent of nationwide chromium emissions from IPCT's.[45] Table 12 also presents nationwide estimates of chromium emissions from CCT's.

TABLE 12. NATIONWIDE COOLING TOWER CHROMIUM EMISSIONS SUMMARY[45,47]

Industry	Total No. of cooling towers	No. of cooling towers using chromate	Cr^{+6} emissions[a] Mg/yr	Tons/yr
Chemical manufacturing	5,096	2,039	43.13	47.54
Petroleum refining	680	476	31.82	35.08
Primary metals	1,118	224	8.39	9.25
Tobacco products	336	16	0.23	0.26
Tire and rubber	267	40	0.18	0.20
Textile finishing	1,018	51	0.08	0.09
Glass manufacturing	58	3	0.01	0.01
Utilities	775	6	0.95	1.05
Subtotal (IPCT only)	9,348	2,855	84.8	93.5
Comfort cooling towers	250,000	37,500	33	34
TOTAL	259,350	40,360	118	128

[a]Based on use of low-efficiency drift eliminators.

4.0 SOURCE TEST PROCEDURES

4.1 CHROMIUM ELECTROPLATING

During the standards support study for hexavalent chromium emissions from hard and decorative chromium electroplating facilities, samples to be analyzed for hexavalent and total chromium were obtained in accordance with EPA Method 5 (40 CFR Part 60-Appendix A), also referred to as Modified Method 13-B in test reports. The only modification to the sample collection method was the elimination of the filter and the replacement of H_2O in the impingers with 0.1 Normal sodium hydroxide. Method 5 provides detailed procedures and equipment criteria and other considerations necessary to obtain accurate and representative emission samples. In order to sample for chromium emissions, Methods 1 through 4 must also be used.

After collection, the samples were analyzed for hexavalent and total chromium (total chromium is the sum of hexavalent chromium plus other chromium). Concentrations of hexavalent chromium were determined using spectrophotometric analysis while total chromium was determined using inductively coupled argon plasmography (ICAP). At the present time, sample analysis has been performed in accordance with the tentative method "Detection of Hexavalent Chromium from Stationary Sources (December 13, 1984)," and a draft method: "E.P.A. Protocol for Emission Sampling for Both Hexavalent and Total Chromium (February 22, 1985)."

4.2 COOLING TOWERS

During the standards support study for chromium emissions from cooling towers, testing was conducted according to two draft test methods developed from previously conducted methods development testing: "Method ___--Determination of Chromium Emissions from Cooling Towers" and "Method ____--Direct Measurement of Gas Velocity and Volumetric Flowrate Under Cyclonic Flow Conditions (Propeller Anemometer)." The cooling tower method is similar to EPA Method 13 (40 CFR Part 60-Appendix A) with the following exceptions: (1) a Teflon™ filter is used in place of a paper filter, (2) a propeller anemometer is used in place of the pitot tube for gas velocity and flowrate measurements, (3) the determination of the measurement site does not follow EPA Method 1, and (4) the chemical

analysis for total chromium in the emission samples is performed using Neutron Activation Analysis (NAA), Graphite Furnace Atomic Absorption (GFAA), or ICAP. In conjunction with the emissions testing, representative cooling tower water samples were collected to determine the ratio of hexavalent to total chromium in the cooling water; these samples were analyzed for total chromium by NAA, GFAA, or ICAP and for hexavalent chromium by the diphenylcarbazide colorimetric method (in "EPA Draft Method-Determination of Hexavalent Chromium Emissions from Stationary Sources," December 13, 1984). The ratio was used to calculate the amount of hexavalent chromium in the cooling tower emissions.

Preliminary material balance calculations were performed on the cooling water at several towers to compare the apparent chromium loss in the drift emissions with the emission measurements obtained during the standards support study. Variables used in these calculations included: cooling water flow rates to the towers, riser cells, and/or fan cells; blowdown rates; makeup water flow rates; addition(s) of chemicals to the cooling water; and chemical analysis of the cooling water samples taken during testing.

Two major modifications were made to the draft test method for cooling towers based on problems encountered and knowledge gained during the testing program. Initially, the draft method specified the use of NAA to determine the total chromium content of the impinger train samples and the cooling water samples. Because of the length of time required for sample analysis and the limited availability of commercial NAA services, two additional analytical techniques, GFAA and ICAP, were utilized and were added as options to the draft test method. Unlike NAA, both of these techniques require acid solubilization of the chromium in the sample prior to analysis. In assessing the chromium recovery efficiency for the concentrated impinger samples from the first test, it was discovered that a significant residue remained in the beakers used to concentrate the samples. The concentration procedure was modified to require an acid rinse of the beakers used for sample concentration with the rinse being added to the concentrated sample.

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